Structural volume change upon photoisomerization of 2,2'-furil: A photoacoustic calorimetric study

Deboleena Sarkar, Alok Chakrabarty & Nitin Chattopadhyay*
Department of Chemistry, Jadavpur University, Kolkata 700 032, India
Email: nitin.chattopadhyay@yahoo.com

Received 8 September 2008; revised 15 December 2008

The cis-skew → trans-planar photoisomerization of 1, 2-di(furan-2-yl)ethane-1, 2-dione (2, 2'-furil), a 1,2-dicarbonyl compound, in the photoexcited triplet state has been investigated by photoacoustic calorimetry in a series of n-alkane solvents at room temperature. The photoisomerization process is associated with a structural volume change of the probe. This has been evaluated and compared with the theoretically calculated volumes of cis and trans geometries of furil. The study reveals that an expansion in volume occurs during the photoinduced isomerization process. In low polarity alkane solvents, electrostrictional contribution to the estimated volume change has been argued to be negligible.

Keywords: Photochemistry, Photoisomerization, Photoacoustic calorimetry, Structural volume change. Furil, Dicarboxyls

The unique structural and photophysical characteristics of 1,2-dicarbonyl compounds have been a matter of interest since long and are being exploited in a number of investigations1-12. These compounds have been found to be considerably flexible, and the large amplitude low frequency vibrational mode associated with the intercarbonyl torsional coordinate has been shown to significantly influence their physicochemical properties13-16. In these compounds the geometry of the molecule is the result of a balance between the steric effects and resonance stabilization. The furanyl analogue of α-dicarbonyls, 2,2'-furil, is considered to be the most flexible among the α-dicarboxyls for two reasons. Firstly, it has five membered substituent rings leading to rotation about the central bond in furil, encountering less hindrance. Secondly, furil has only one proton in each ring capable of interacting sterically with the carbonyl oxygen. This ground-state conformation of furil is assigned to a nonplanar or cis-skew geometry8-14,17. Under frozen condition this nonplanar or cis-skew geometry predominates even in the excited triplet state. In fluid medium, this nonplanar geometry relaxes to a trans-planar geometry8. This particular step is the cis-skew to trans-planar conformational relaxation process. Singh and Palit9, however, disregarded such a relaxation process in the excited state of furil and proposed that in the excited state there was only one conformer. In frozen matrix at 77K, furil has three emission bands at 470, 525 and 570 nm. The emission band at 470 nm is utterly destroyed when a chopper is used confirming this emission to be fluorescence. At room temperature, however, the fluorescence of furil is found to be too weak to interfere with the photoacoustic calorimetric (PAC) response. The 525 and 570 nm bands are attributed to phosphorescence. The relative intensities of 525 and 570 nm bands are not sensitive to solvent polarity18. Sandroff and Chan8 reported a blue shifted emission band due to the non-planar furil molecule in addition to the emission from the planar one in furil doped benzophenone crystal at 95 K. Based on the literature reports the triplet photophysical behavior of furil has been represented in Scheme 1.

To the best of our knowledge, no photoacoustic calorimetric study on furil has been reported till date. The optimized structures of the skew and the trans
conformations of furil designate an intrinsic volume change due to photointerconversion. Photoacoustic calorimetry (PAC) or laser induced optoacoustic spectroscopy (LIOAS), a photothermal technique, is the easiest and the most reliable method for the estimation of the structural volume change associated with such a photointerconversion. A classic review article by Braslavsky and Heibel throws light on this relatively newly developed photothermal technique. Very fast non-radiative deactivation of the photoexcited fluorophore leads to the release of a reasonable amount of heat to the solvent molecules surrounding it. Dissipation of the released heat through the solvent is a much slower process resulting in a heating effect in the microscopic region. This leads to an adiabatic expansion of the volume of the solvent molecules, present in the immediate vicinity of the excited fluorophore. This is known as thermoelastic expansion, which generates a shock wave and finally develops an acoustic wave. A high frequency transducer, placed on the wall of the LIOAS cell at a right angle conformation to the direction of the laser light, picks up the ultrasonic acoustic signal which is then amplified and fed to a digitizer and finally to a computer.

PAC technique yields information about the volume changes associated with an excited state photoprocess of a sample relative to that from a suitable reference. The PAC signal of a sample may be represented as Eq. 1.

\[ S = k [\Delta V_{th} + \Delta V_R] \quad \ldots (1) \]

where \( S \) is the amplitude of PAC signal. Two possible contributions can be ascribed to the volume change with a photoinduced reaction in solution: (i) the change in reaction volume (\( \Delta V_R \)), and (ii) the expansion of the medium upon release of the heat (\( \Delta V_{th} \)). \( \Delta V_R \) is independent of temperature as well as the thermoelastic properties of the medium, at least to the first approximation. \( \Delta V_{th} \) is a function of temperature and depends on the thermoelastic parameter \( (c_p \beta / \beta) \) of the solution, where \( c_p \) is the specific heat capacity at constant pressure; \( \rho \) is the density of the solution = density of solvent for dilute solutions, and \( \beta = 1/V \frac{\partial V}{\partial T} \rho \), the volume expansion coefficient and \( k \) is a constant that takes care of the geometrical and instrumental parameters. These two volume contributions can be separated from the PAC measurements as a function of the thermoelastic parameters of a series of solvents with similar properties. A reaction volume in solution has two components, the structural volume change related to the size of the reactant and product, and the volume change associated with solvation. The latter is often known as electrostriction and is related to medium polarity and dipole interactions. For ionic solutes in polar solvents the electrostriction is often significant and sometimes it utterly overrides the structural volume component.

Fessenden et al. showed that furil has a very low dipole moment in the triplet state. Also, an insignificant contribution of electrostriction for a similar situation has been referred to by Williams et al. Herbrich and Schmidt assigned the contribution of electrostriction to the volume change due to photoisomerization and the thermoelastic parameter of the solvent for \( n \)-alkanes. They suggested that the contribution due to electrostriction to the volumes and enthalpies determined by PAC can be eliminated by using a series of \( n \)-alkanes.

In the present work, we have exploited PAC technique to determine the structural volume change of furil for the non-planar or cis-skew \( \rightarrow \) trans-planar conformational transformation in a series of \( n \)-alkane solvents. Dual phosphorescence from furil, one in the frozen state and the other in fluid medium, indicates the existence of at least two different conformations of furil in the excited triplet state. The volume change due to electrostriction is ignored considering firstly, the very low polarity of the probe itself in either states, and, secondly the use of low polarity \( n \)-alkane solvents as the media. thermoelastic parameter, however, varies with a variation in the chain length of the different \( n \)-alkanes in the series. The structural volume change obtained from the experiment is in agreement with that calculated from the optimized non-planar and the \( trans \)-planar conformations of the molecular system.

**Experimental**

Furil and 2-hydroxy benzophenone (HBP) were obtained from Aldrich and recrystallized from methanol. Normal alkanes, namely, pentane (PEN), hexane (HEX), heptane (HEP), octane (OCT), decane (DEC), dodecane (DOD), and hexadecane (HEXD), were all highest purity Aldrich products (spectrophotometric grade) and were used as received.

In each alkane solvent three solutions of furil and HBP were prepared with absorbance values of 0.08, 0.10 and 0.12. Each solution was degassed by bubbling for 15 minutes with ultrapure nitrogen gas.
that had been saturated with the alkane prior to the entry in the PAC cell. The solutions were excited by the third harmonic (355 nm) of the INDI-40 Nd:YAG laser system from Spectra Physics (USA) operating at 10 Hz repetition rate. Laser energy was measured by a laser energy meter FieldMax-II, fitted with energy sensor J8LP-4 (both from Coherent). The fluence-normalized PAC signal intensity ratios ($S_S/S_R$) were determined for the three solutions in a particular solvent and the average value was calculated. The diameter of the laser beam was set to 1 mm using a pinhole. The range of laser energy used spanned between $0 - 30 \mu$J to avoid any biphotonic process or ground state depletion. The acoustic wave was detected with a piezoelectric transducer (2.25 MHz, from Panametrics) attached to the wall of the long neck quartz cuvette with 1 cm optical path length. The ultrasonic acoustic signal was amplified by a ultrasonic preamplifier (Panametrics-5676) and fed to a digital oscilloscope (Tektronix-2012) and finally to a computer. Vacuum grease was used between the wall of the cuvette and the transducer face to avoid the disturbances due to the interference of the layer of air trapped therein. Average of 64 signals was stored in the oscilloscope.

Theoretical calculations on furil were performed on semi-empirical AM1-SCI basis using the commercial package Hyperchem 6.0.

**Results and discussion**

**Theory**

The ground state geometry of the furil molecule was optimized by semi-empirical AM1 method$^{36,37}$. The energy ($E_0$), dipole moment in the ground state, the transition energies ($\Delta E_{i\rightarrow j}$), and dipole moments of different excited states of furil were obtained through AM1-SCI (singly excited configuration interaction) method. More than 100 configurations have been taken within an energy window of 13 eV from the ground state. Orbitals and one-electron density matrices were generated using the CI wavefunctions, which were then used to calculate the dipole moments of the excited states of furil. The potential energies of different electronic states of furil were calculated as a function of the torsion angle between 2-6-11-13 (Scheme 2) from $0^\circ$ to $180^\circ$. From the calculation it was revealed that in the ground state ($S_0$) furil has a cis-skew conformation with two-carbonyl moieties making an angle near to $100^\circ$ and in the excited triplet state ($T_1$) it has a stable trans-planar conformation with an angle of nearly $180^\circ$.

A glance at the optimized structures excludes the possibility of furil to be considered spherical. We therefore calculated the volumes of these optimized conformations considering them cylindrical. For both the isomers, the length of the cylinder was taken from H9 to H19 and the diameter (2$r$) of the cylinder from H18 to H20 (Scheme 2). For the cis-skew isomer, the length is obtained as $8.37\AA$ and for the trans one it is $10.03\AA$. Diameter for both the isomers is calculated to be the same and it is $4.38\AA$. The required volumes were calculated from these dimensions. Since in the excited state furil undergoes relaxation from cis-skew to trans-planar form, volume change was estimated as $\Delta V = (V_{trans} - V_{skew})$. The volume change is found to be positive and is equal to $15.06\text{ mL/mol}$. As expected, the optimized structures suggest an increase in the volume for the skew $\rightarrow$ trans phototransformation.

**PAC studies**

The principle of PAC technique has already been described in detail in a number of articles$^{19,20,24,27-29}$. The photoacoustic signals of the sample (furil) and the calorimetric reference (HBP) were recorded varying the laser energy from 0 to $20 \mu$J. Typical LIOAS signals of furil and the reference are shown in Fig. 1.

From the PAC signals of furil and HBP (Fig. 1), there is no indication of any resolvable kinetics. Hence, deconvolution of the signal was considered unnecessary in the present case; rendering the use of energy-normalized signal amplitudes only ($S_n$)$^{38}$. 

---

**Numbered general structure and skew and trans conformations of furil**

Scheme 2
The plots of first maximum of the LIOAS signal versus laser energy were found to be linear in all the solvents. This linearity confirms non-occurrence of any biphotonic process or ground state depletion of the compounds under study\(^{39,40}\). Figure 2 presents a set of these plots for the sample and the reference.

The photoacoustic or LIOAS signal from the sample comprises the contribution of prompt heat released by the sample and any volume change associated with the photoprocess within the heat integration time. For the reference HBP, the fraction of the absorbed energy coming out as heat ($\alpha$) is 1.0 (refs. 29,40). Moreover, HBP itself does not involve any structural volume change under the experimental condition ($\Delta V_R = 0$). Therefore, for the reference HBP, the signal depends only on the prompt heat released multiplied by the thermal expansivity of the solvent. For HBP, Eq. (1) takes its simplified form as

$$S_R = k \left[ \Delta V_{th} \right] = k\alpha E_\lambda \beta / (c_p \rho)$$

...(2)

where $S_R$ is the amplitude of reference signal, $E_\lambda$ is the excitation energy per mole of photons. Since for HBP, $\alpha = 1$, Eq. (2) reduces to,

$$S_R = k \left[ \Delta V_{th} \right] = kE_\lambda \beta / (c_p \rho)$$

...(3)

However, for the sample furil, there is an extra contribution from the structural volume change ($\Delta V_R$) associated with the photoisomerization process and the amplitude of the photoacoustic signal is given by Eq. 4,

$$S_S = k \left[ \Delta V_{th} + \Phi R \Delta V_R \right] = k \left[ \Delta V_{th} + \Phi R \Delta V_R \right]$$

...(4)

where $S_S$ is the amplitude of sample signal and $\Phi R$ is the photoisomerization quantum yield of furil in the excited triplet state. When the sample solution and reference solution have the same absorbance, the ratio of Eqs (4) and (3) will produce,

$$\left( S_S / S_R \right) = \alpha + (\Phi R \Delta V_R / E_\lambda) (c_p \rho / \beta)$$

...(5)

where the ratio ($S_S / S_R$) is the fluence-normalized optoacoustic signal of furil ($S_S$) with respect to that of HBP ($S_R$). The values ($S_S / S_R$) were determined in each $n$-alkane solvent with three different values of absorbances (0.08, 0.10 and 0.12) and the mean values were taken. The LIOAS data of furil is produced in Table 1.

A plot of mean values of ($S_S / S_R$) versus the thermoelastic parameter of the alkane solvents, ($c_p \rho / \beta$), is found to be linear (Fig. 3). The structural...
volume change per mole ($\Delta V_R$) is extracted from the slope of the plot. The positive slope (6.0 \times 10^5 \text{ mL/J}) is indicative of a volume expansion due to the conformational change of furil in the excited state. The experimental value of ($\Phi_R \Delta V_R$) is calculated to be

$$20.2 \pm 1.1 \text{ mL/mol using the value of } E_\alpha = 3.37 \times 10^5 \text{ J/mol at the excitation wavelength of 355 nm.}$$

For the aromatic diketones, the fluorescence quantum yield to be unity.

Thus, assuming $\Phi_R \sim 1$, $\Delta V_R$ comes out to be

$$20.2 \pm 1.1 \text{ mL/mol.}$$

It is pertinent to mention here that the fluorescence quantum yield of furil in different alkane solvents does not vary significantly. As discussed above, the estimated $\Delta V_R$ can be directly assigned to the structural volume change, since under the experimental condition with furil in low polarity solvents the electrostriction is insignificant. The estimated value of the structural volume change is in agreement with the value of 15.06 mL/mol calculated from the optimized cis-skew and trans-planar geometries of furil. The study reveals that the skew $\rightarrow$ trans photoisomerization leads to an expansion in volume in the triplet state of furil.

**Acknowledgement**

Financial support from DST (Project No. SR/S2/LOP-13/2004), and CSIR, Govt of India, is gratefully acknowledged. DS thanks CSIR for a research fellowship.

**References**